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(21) International Application Number: PCT/US95/00151 (22) International Filing Date: 6 January 1995 (06.01.95) (30) Priority Data: 08/185,598 21 January 1994 (21.01.94) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: SCANLAN, Thomas, J.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). ZENDER, Mark, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: ALLEN, Gregory, D. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STARVED MATRIX COMPOSITE (57) Abstract <p>A composite that includes ceramic filler particles in a carbonaceous matrix arranged in the form of a starved matrix microstructure having a surface available for coating; and a coating of a material selected from the group consisting of silicon carbide, silicon nitride, and combinations thereof on at least a portion of the surface of the microstructure.</p> <div style="text-align: center;"> </div>		

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STARVED MATRIX COMPOSITEBackground of the InventionField of the Invention

This invention relates to composites based upon a
10 starved matrix microstructure and parts prepared therefrom.

Description of the Related Art

Porous ceramic composites are known. Porous
composites have been suggested for use as filters (e.g.,
15 for molten metal, diesel engine exhaust, and hot gas),
catalyst supports, and sound damping equipment (e.g.,
mufflers). Because many of these applications entail
exposure to relatively high temperatures, it is desirable
for the composites to exhibit good high temperature
20 resistance. It is also desirable for the composites to be
able to withstand repeated heating and cooling cycles
without compromising structural integrity.

Summary of the Invention

25 In general, the invention features a composite that
includes (a) ceramic filler particles in a carbonaceous
matrix arranged in the form of a starved matrix
microstructure having a surface available for coating; and
(b) a coating of a metal selected from the group consisting
30 of silicon carbide, silicon nitride, and combinations
thereof on at least a portion of the surface of the
microstructure.

Preferred filler particles are substantially
spherically-shaped and/or hollow particles. Examples of
35 particularly preferred particles are aluminosilicate solid
spheres and aluminosilicate hollow spheres. The average

5 size of the filler particles typically ranges from about 10 to about 500 micrometers, preferably from about 10 to about 250 micrometers. Typically, glass or glass-ceramic filler particles do not soften or melt at temperatures up to at least 900°C, more preferably up to at least 1000°C.
10 Further, typically crystalline ceramic filler particles do not soften or melt at temperatures up to at least 900°C, more preferably up to at least 1000°C.

The porosity of the composite preferably ranges from about 20 to about 60% (as measured by the water
15 absorption method described infra), more preferably from about 30 to about 40%. The coating consisting of silicon carbide, silicon nitride, or combinations thereof, preferably is present in an amount ranging from about 25 to 35% by weight based on the total weight of the composite.

20 A preferred method of making composites according to the invention includes the steps of:

(a) forming an article having a starved matrix microstructure with a surface available for coating from a mixture comprising ceramic filler particles and an organic
25 polymer binder;

(b) pyrolyzing the article of step (a) to carbonize the binder while retaining the starved matrix microstructure of the article; and

(c) depositing a coating of a material selected
30 from the group consisting of silicon carbide, silicon nitride, and combinations thereof on at least a portion of the surface of the microstructure of the article to form the composite.

A more preferred method of making composites
35 according to the invention includes the steps of:

5 (a) providing a mixture comprising ceramic filler particles and a curable organic polymer binder wherein upon curing the curable organic polymer binder an article having a starved matrix microstructure with a surface available for coating is formed;

10 (b) curing the curable organic polymer binder of the mixture to provide an article having a starved matrix microstructure with a surface available for coating;

 (c) pyrolyzing the article of step (b) to carbonize the binder while retaining the starved matrix
15 microstructure of the article; and

 (d) depositing a coating of a material selected from the group consisting of silicon carbide, silicon nitride, and combinations thereof on at least a portion of the surface of the microstructure of the article to form
20 the composite.

 Preferably, the binder is an epoxy resin, phenolic resin, or combination thereof. The method can further include applying a second organic binder to the article prior to step (b).

25 The silicon carbide, silicon nitride, or combination thereof, is preferably deposited by chemical vapor deposition.

 In this application:

 "ceramic particles" refers to glass, glass-ceramic,
30 and/or crystalline ceramic particles;

 "carbonaceous" refers to a carbon matrix or coating wherein substantially all of the carbon is amorphous;

 "starved matrix microstructure" refers to a microstructure in which the ceramic filler particles are
35 interconnected by the organic polymer binder (or carbonaceous material) such that pores (voids) are present

5 between the particles, providing an overall porous structure;

"porosity of the composite" refers to the voids formed between adjacent filler particles by the carbonaceous matrix necking between particles;

10 "coating" refers to a layer of silicon carbide, silicon nitride, or combination thereof deposited on at least a portion of the surface of the starved matrix microstructure available for coating;

"surface of the starved matrix microstructure
15 available for coating" refers to any portion of the composite upon which silicon carbide, silicon nitride, or combination thereof can be deposited. Such surface includes the surface of filler particles coated with carbonaceous material, portions of the surface of filler
20 particles lacking a coating of carbonaceous material, and the surface of the carbonaceous matrix itself (e.g., the necks interconnecting the filler particles).

Composites according to the present invention are useful in a variety of applications, particularly where
25 temperatures of greater than about 500°C are encountered. Such applications include filtration (e.g., applications requiring filtration of suspended or dispersed particles from a high temperature gas stream such as refinery process gas streams or combustion gases). The composites may also
30 be useful for filtering particles from molten metals or corrosive fluids.

The composites can also be used as a support material for catalysts. Examples of suitable catalysts include conventional catalysts such as metals (e.g.,
35 ruthenium, osmium, rhodium, iridium, nickel, palladium, and

5 platinum) and metal oxides (e.g., vanadium pentoxide and titanium dioxide).

The composites are also particularly useful in applications involving the transport of hot gases. To this end, the composites could be shaped into furnace components
10 such as burner nozzles, radiant burner tubes, and air recuperators.

Another application that takes advantage of the high temperature stability (i.e., above about 500°C) of the composites is kiln furniture. Kiln furniture refers to the
15 support structures in a furnace which hold parts to be fired in a kiln. Composites according to the invention are useful as kiln furniture because, for example, they have a low thermal mass, a high structural integrity (i.e., they maintain dimensional stability at high temperatures under
20 load), are non-contaminating (i.e., surface particles are resistant to flaking or spalling), and can distribute heat effectively.

Other applications for which the composites are useful including sound attenuation (e.g., mufflers and
25 acoustic barriers) and microwave absorption (e.g., in the pre-heating of catalytic converters).

Description of the Preferred Embodiments

Brief Description of the Drawing

30 The FIGURE is an enlarged view of the starved matrix microstructure found in composites according to the invention.

Referring to the FIGURE, composite according to the invention 10 has a starved matrix microstructure in which
35 ceramic filler particles 12 having a surface available for coating are interconnected by carbonaceous necks 14 (formed

5 upon pyrolysis of an organic polymer binder) such that
voids (pores) 16 exist between particles, resulting in an
open, porous structure. A coating of silicon carbide,
silicon nitride, or combination thereof 18 is deposited on
at least a portion of the microstructure surface available
10 for coating but preferably does not clog the pores 16 of
the composite.

The ceramic filler particles must be resistant to
high temperatures (i.e., resist softening (which results in
deformation) or melting at temperatures up to at least
15 900°C, and more preferably up to at least 1000°C). The
preferred particles are substantially spherically-shaped
because such particles minimize the density of the final
composite part, leading to lightweight composite parts.
Hollow spherical particles (bubbles or microbubbles) are
20 particularly preferred because they further minimize
composite density.

The particles can range in size from about 10
micrometers to several millimeters, though the size range
preferred in the practice of the invention is from about 10
25 micrometers to about 1000 micrometers, more preferably from
about 10-500 micrometers, and even more preferably from
about 10-325 micrometers. It is generally preferred to
minimize the size distribution as this tends to maximize
the porosity of the composite.

30 Examples of suitable particles for use in this
invention include hollow aluminosilicate bubbles
commercially available under the trade designation
"EXTENDOSPHERES" from PQ Corporation, Valley Forge, PA (10
to 350 micrometers in size) and "Z-LIGHT" bubbles
35 commercially available from Zeelan Industries, St. Paul, MN
under the product designations "W1012 Z-Light", "W1200 Z-

5 LIGHT", "W1600 Z-LIGHT," "W1000 Z-LIGHT", "G3400 Z-LIGHT",
and "G3500 Z-LIGHT". These bubbles are available in
different size ranges. Solid aluminosilicate spheres
sold, for example, under the trade designation
"ZEEOSPHERES" from Zeelan Industries, St. Paul, MN are also
10 useful, particularly in the preparation of higher density
composite materials. Oxide and non-oxide ceramic bubbles
such as those prepared by the methods described in U.S.
Patent No. 5,077,241 having sizes ranging from about 1 to
300 micrometers are suitable as well.

15 Additional examples of suitable fillers are
composite ceramic spheres having closed cell porosity
commercially available under the trade designation
"MACROLITE CERAMIC SPHERES" from Kinetico Inc., Newbury,
OH. These composite spheres are available in sizes ranging
20 from 200 to 600 micrometers. Particularly preferred are
"Macrolite ceramic spheres" commercially available under
the trade designation "ML 40/60" having sizes ranging from
200-400 micrometers.

The particles are bonded together by means of an
25 organic polymer binder in a starved matrix microstructure
(i.e., the binder forms necks between the particles but
leaves substantial voids between the particles, leading to
a porous composite). The polymer binds the particles while
maintaining a starved matrix configuration. Examples of
30 suitable organic polymer resins (which may be in the form
of powders or liquid solutions) include epoxies, phenolics,
polyethylenes, polypropylenes, polymethylmethacrylates,
urethanes, cellulose acetates, polytetrafluoroethylene
(PTFE), and natural and synthetic rubbers. The preferred
35 binders for use in this invention are phenolics and
epoxies.

5 One preferred epoxy resin for use in this invention
is a powdered resin commercially available under the trade
designation "SCOTCHCAST 265" from the 3M Company. Suitable
phenolic resins include both acid catalyzed and base
catalyzed phenolic resins. Examples of commercially
10 available phenolic resins include phenolic resins sold
under the trade designations "DUREZ" from Occidental
Chemical Corp., Dallas, TX; "DURITE-SC-1008" from Borden
Chemical, Columbus, OH; and "BKUA-2370-UCAR" (a water-based
phenolic resin solution) from Union Carbide, Danbury, CT.
15 The viscosity of the resin can be adjusted by adding a
compatible organic solvent such as acetone or methanol to
the resin, or by adding water to a water-based phenolic
resin solution.

Other materials can be added to the resin/filler
20 particle mixture as well. For example, it may be desirable
to add chopped or continuous fibers (e.g., ceramic fibers)
to the mixture, or to form the composite in a mold lined
with reinforcing fabric (e.g., ceramic mesh) in order to
improve properties such as thermal shock resistance and
25 toughness. Examples of suitable additives include fibers
or fabric of aluminoborosilicate commercially available
under the trade designations "NEXTEL 312" and "NEXTEL 440"
from the 3M Company, St. Paul, MN and aluminosilicate
fibers or fabric commercially available under the trade
30 designation "NEXTEL 550" from the 3M Company.

Hollow carbon microspheres such as those
commercially available under the trade designation
"CARBOSPHERES" from Carbospheres Specialty Products, Inc.,
Fredericksburg, VA can also be added. If desired, these
35 microspheres can be burned out under controlled conditions
after being added to the resin/ceramic particle mixture by

5 firing in an oxidizing atmosphere. This process would create voids in the composite, thereby increasing porosity. Polymeric microspheres can be burned out as well.

Preferably, composite parts according to the invention are prepared by mixing filler particles with a
10 resin binder and other (optional) desired additives in a twin shell blender. After mixing for a time sufficient to blend the ingredients, the mixture is poured into a mold having a desired shape. To promote removal of the composite part from the mold, the mold is preferably
15 treated with a release agent such as a fluorocarbon, silicone, talcum powder, or boron nitride powder. The mixture is then heated in the mold. The particular temperature of the heating step is chosen based upon the resin binder. In the case of epoxy and phenolic resins,
20 typical temperatures are about 170°C. For large parts or parts having complex shapes, it is desirable to ramp the temperature up to the final temperature slowly to prevent thermal stresses from developing in the heated part.

After heating, the composite part is removed from
25 the mold. If desired, additional resin can be applied to the composite part (e.g., by dipping or brushing). Preferably, this resin is different from the resin in the initial mixture. For example, where the resin in the initial mixture is epoxy resin, an additional coating of
30 phenolic resin may be applied to the composite part. The composite part is then heated again.

Once the part is removed from the mold, the composite part may be further shaped by machining or used as is. For example, the part can be sectioned into discs
35 or wafers. The part can also be provided with holes or cavities. For example, it is known in the art to provide

5 holes in kiln furniture to facilitate flow of gas and to
reduce weight. For example, holes would be used to bolt
pieces together or to attach parts to a furnace wall. The
composite part is then placed in a furnace (e.g., a
laboratory furnace) provided with an inert (e.g., nitrogen)
10 or reducing gas (e.g., hydrogen) atmosphere to pyrolyze the
binder. Typically the pyrolysis is carried out at
atmospheric pressure. The particular pyrolysis temperature
is chosen based upon the binder. For epoxy and phenolic
binders, typical pyrolysis temperatures range from 500 to
15 1000°C. The composite part is loaded into the furnace at
room temperature and the furnace temperature then ramped up
to the final pyrolysis temperature over the course of a few
hours (a typical ramp cycle is about 2.3 hours).

During pyrolysis, the starved matrix microstructure
20 is preserved and the binder is converted into carbonaceous
material. The carbonaceous material typically covers the
surfaces of the ceramic filler particles and forms necks
between adjacent particles, thereby producing a
carbonaceous matrix throughout the part. This carbonaceous
25 matrix forms part of the surface available for coating with
silicon carbide and/or silicon nitride. It is further
expected that some of the particles will have portions
where no carbonaceous material is covering them due to the
way in which the binder coats them and forms between them.
30 The uncoated surface of these particles can be coated with
silicon carbide and/or silicon nitride as well. Generally,
however, it is preferred that at least 50% (more
preferably, at least 90%) of the surface available for
coating be provided with carbonaceous material.

35 Following pyrolysis, the composite part is removed
from the furnace for coating with silicon carbide, silicon

5 nitride, or combinations thereof. The coating can be formed from solution precursors such as polysilazanes dissolved in organic solvents. Moreover, in the case of silicon carbide, the coating can be formed by reaction of molten silicon metal with carbon from the carbonaceous
10 matrix of the pyrolyzed composite part. However, it is preferred to deposit the coating by chemical vapor deposition (CVD) of gaseous precursors at reduced pressures according to techniques well-known in the art. Suitable commercially available silicon carbide precursors for this
15 purpose include dimethyldichlorosilane ("DDS") and methyltrichlorosilane ("MTS"). Suitable commercially available silicon nitride precursors for this purpose include ammonia, silicon tetrachloride, and hydrogen.

The aforementioned deposition techniques can also
20 be used in combination with each other.

In a typical CVD coating process, the pyrolyzed composite part is placed in a chemical vapor deposition chamber (e.g., a quartz chamber), which is then evacuated to a pressure in the range from about 5 to about 50 torr.
25 While flowing a non-oxidizing (e.g., hydrogen) gas through the evacuated chamber, the furnace is heated (e.g., resistively or inductively) to the carbonization temperature of the precursor. The precursor (e.g., DDS or MTS in the case of silicon carbide) is then introduced into
30 the chamber, typically by bubbling a non-oxidizing gas through the precursor in the case of volatile liquid precursors or by independently introducing a gaseous precursor into the chamber through a separate gas line.

The gas flow rates and deposition rate are selected
35 to ensure that the porous structure of the part is maintained. The preferred flow rates of the precursor and

5 non-oxidizing gas are chosen based upon the size of the furnace chamber. For example, the preferred flow rates for a 56 cm diameter by 61 cm deep CVD chamber are about 9 to 80 slpm (standard liters per minute) for the non-oxidizing gas and from about 3 to about 16 slpm for the precursor.
10 Typically, deposition times range from about 5 to about 24 hours.

After deposition of the coating, the power is turned off and hydrogen is admitted into the chamber for about 0.5 hours, after which the furnace is filled with an
15 inert gas (e.g., nitrogen or argon) and typically cooled for at least 8 hours before removing the coated composite parts.

Composite parts having different shapes and sizes can be produced during one run in the CVD chamber. The
20 parts should fit in the CVD chamber with sufficient space (i.e., about 1 cm or greater) around them to allow for the adequate flow of gases. This assures even distribution of the reactant gases and thus uniform deposition of silicon carbide, silicon nitride, or combinations thereof.
25 Further, the composite parts can be set onto a plate having many holes in it to allow for flow through and mixing of the reactant gases. Alternatively, the composite parts can be hung from a holder at the top of the chamber.

The desired amount of the coating deposited is
30 chosen based upon the particular application for which the part is intended to be used. The amount can be adjusted over a wide range (e.g., 10 to 150 weight percent) based on the total composite weight. Preferably, however, the amount deposited ranges from about 25-35 weight percent
35 based on the total composite weight. The coating may be

5. deposited on all or a portion of the microstructure surface available for coating.

The porosity of the composite can vary depending, for example, upon the size and size distribution of the filler particles, as well as the amount of polymer used for the matrix. Preferably, the porosity ranges from about 20 to about 60 percent, more preferably from about 30 to about 40 percent. Porosity is measured using a water absorption method. Dry composite parts are weighed and then placed in a vacuum desiccator with sufficient water to cover the part. The pressure to the container is then reduced to remove the air from the pores and force water into the open pores of the structure. The vacuum is turned off after about two hours and the water-saturated composite part is removed from the vacuum jar and weighed. The weight of the water incorporated into the composite part is divided by the volume of the composite part to determine the percent porosity. In determining porosity, any hollow filler particles are treated as solid particles; thus porosity is a measure of the voids formed between adjacent filler particles by necking of the carbonaceous matrix.

The composite parts can be tested as sound damping materials by installing the part in the muffler housing of a 1/4 horsepower air motor (commercially available under the designation "Gast Model #2AM-NCC-16" from Gast Manufacturing of Benton Harbor, MI) set at an operating speed of 4000 RPM. A similar test may also be run using the muffler housing from a 3.5 horsepower engine commercially available from Briggs and Stratton. Measurement of noise level (i.e., sound pressure) is accomplished by means of a hand-held sound level meter (commercially available from Lucas Cel Instruments, Severna

5 Park, MD) positioned 1 meter from the sound source at an angle of 45° from the direction of the sound source. The units of measurement are in dBA, which refers to an A-weighted decibel scale. The noise measurement is then compared under the same conditions to the muffler
10 originally installed in the motor.

Back pressure (measured in MPa or psi) is the pressure difference across the part (i.e., the pressure at the inlet minus the pressure at the outlet). Flow is measured in standard cubic feet per minute (scfm) or
15 standard liters per minute (slpm), which requires measurement of temperature, as well as the flow rate, so that the flow rate can be normalized to 25°C. Back pressure of a cylinder or disc of the composite material is tested at various flow rates on a laboratory flow bench. A
20 muffler housing is connected to a laboratory pressurized air line by means of metal tubing. The temperature of the inlet air is measured with a thermometer. A gauge pressure sensor is placed in line between the air inlet and the muffler to measure the build-up of back pressure from the
25 muffler. Use of a flow bench to measure back flow, rather than a muffler mounted on an engine, permits measurement of the reduction in sound due only to the muffler (as opposed to other engine noises).

Objects and advantages of this invention are
30 further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to limit this invention. All parts and percentages are by weight unless otherwise indicated.

35

5

EXAMPLES

Example 1

This example illustrates the preparation of a cylindrically-shaped composite part according to the invention.

4.66 parts by weight aluminosilicate spheres ranging in size from 150 micrometers to 350 micrometers (commercially available under the trade designation "Z-LIGHT W1600" from Zeelan Industries of St. Paul, MN) and 1 part by weight epoxy resin (commercially available under the trade designation "SCOTCHCAST 265" from the 3M Company, St. Paul, MN) were mixed together in a twin shell blender; the resulting mix was then used to fill several cylindrical aluminum molds. Each mold was open at the top, had a removable bottom, and measured 5.08 cm in diameter x 10.16 cm in length. Each mold was treated with a fluorocarbon release agent (commercially available under the trade designation "REN RP79-1" from Ciba Geigy Corp. of East Lansing, MI) prior to filling.

Each filled mold was placed in an oven at 170°C for 2 hours to cure the epoxy resin. The cured cylindrically shaped product was then removed from the mold while still warm and cooled to ambient temperature in air. The porosity of the cured part was measured by the water displacement method (described above) to be about 35%.

Next, the epoxy resin was pyrolyzed by placing the cured part in an inert atmosphere (nitrogen) furnace (commercially available under the trade designation "Rapid Temp Type 1620E" furnace from CM Inc. of Bloomfield, NJ). The furnace was flushed with nitrogen before ramping up the temperature to 1000°C over the course of 2.3 hours. The

5 1000°C temperature was held for 1.5 hours, and then allowed to drop to room temperature.

Following pyrolysis, the part was placed in a separate chamber for coating with silicon carbide via chemical vapor deposition (CVD). The silicon carbide was
10 deposited at a temperature of about 1000°C for a period of 3 hours and 40 minutes. The pressure was not allowed to rise above about 10 torr; the flow rates were set at approximately 40 slpm (standard liters per minute) hydrogen; 30 slpm nitrogen; and 10 slpm
15 methyltrichlorosilane (MTS).

After cooling to room temperature in the CVD chamber overnight, the part was removed from the furnace and examined. The porosity of the coated part was about 33.3% (as measured by the water displacement method
20 described above). The total weight of silicon carbide added was determined to be 25 grams.

A cross-section of the part was examined by scanning electron microscopy. The silicon carbide appeared to be coated throughout the cylinder; the coating was
25 thicker at the outer edges, decreasing in thickness toward the center of the part.

Example 2

This example illustrates the preparation of another
30 cylindrically-shaped composite part according to the invention useful as a muffler.

A sample was prepared as described in Example 1, except that upon release from the mold after the curing step the part was dipped into an aqueous solution of
35 phenolic resin. This resin solution was prepared by diluting 1 part phenolic resin solution (commercially

5 available under the trade designation "BKUA 2370", from Union Carbide of Danbury, CT, 45% phenolic in water) with 10 parts methanol. The coated cylinder was then placed into an oven and heated for 1 hour at 200°C to evaporate solvent and cure the phenolic resin. Pyrolysis of the
10 phenolic and epoxy resin and silicon carbide deposition were then carried out as described in Example 1.

The resulting part was tested as described above for utility as a muffler on a 3.5 horsepower Briggs & Stratton engine. It showed a sound reduction of 3-5 dBA
15 over the muffler which was installed in the engine by the manufacturer.

The back pressure of the part was also tested at room temperature using a laboratory flow bench at 50 scfm (1415 slpm). The part had a back pressure of 5 psi (0.034
20 MPa), which compared favorably with the back pressure of the as-installed muffler (which was 3.5 psi (0.024 MPa)). When tested under flow bench conditions, the part also showed a reduction in sound pressure of 20 dBA over the muffler installed by the manufacturer.

25

Example 3

This example illustrates the preparation of yet another cylindrically-shaped composite part according to the invention useful as a muffler.

30 Ceramic particulate spheres ranging in size from 200 to 400 micrometers (commercially available under the trade designation "MACROLITE 4060 ceramic spheres" from the 3M Company) were placed in a plastic bag and mixed with 2% by weight water until the particles were wet out, as
35 determined by a uniform appearance among the spheres. One part by weight of epoxy resin ("SCOTCHCAST 265") was then

5 added to 8 parts by weight of the moist spheres and the resulting mixture stirred by hand until the resin was uniformly distributed. Wetting out with water appeared to promote adhesion of the resin to the spheres.

10 Next, this mixture was used to fill a cylindrically-shaped mold having an open top, a removable bottom, and measuring 3.17 cm in diameter x 15.24 cm in length. The mold was treated with a fluorocarbon release agent ("REN RP79-1") before filling. The filled mold was then placed in a 170°C oven for 2 hours to cure the epoxy
15 resin. Following cure, the mold was removed from the oven and the sample removed from the mold while warm by pushing it out the open end of the mold. The cured part had a porosity of about 35% (as measured by the water displacement method described above).

20 A band saw was used to cut discs from the cylindrically-shaped part having thicknesses ranging from 0.63 cm to 2.54 cm. The discs were then pyrolyzed in a furnace under a nitrogen atmosphere at 260°C for 1 hour, held for 15 minutes at that temperature, then heated to
25 593°C for 1 hour and held there for 15 minutes. Afterwards, the furnace was allowed to cool for 8-12 hours to less than 149°C before the chamber was opened and the samples removed.

30 Some of the discs had cracks in them and were not processed further. Those discs which remained intact were coated with silicon carbide via chemical vapor deposition as described in Example 1. The porosity of a representative disc was 34% (as measured according to the water displacement method described above).

35 After coating with silicon carbide, a representative disc was tested for noise reduction in an

5 air motor. A 0.95 cm thick disc was placed in the muffler housing of a 1/4 horsepower air motor (commercially available under the designation Gast Model #2AM-NCC-16 from Gast Manufacturing, Benton Harbor, MI) set at an operating speed of 4000 RPM. The sound pressure level was measured
10 for the muffler of the invention at a distance of 1 meter, 45° from the source using a sound level meter (available from Lucas Cel Instruments, Severna Park, MD) and compared under the same conditions to the cloth muffler that was originally installed on the motor. The muffler according
15 to the invention had a sound level of 71 to 72 dBA, whereas the cloth muffler (about 1.25 cm thick) originally installed in the air motor had a sound level of 80 to 84 dBA. The 8 to 13 dBA reduction in noise represents approximately a 6 to 20 times reduction in sound power
20 output.

The variation in back pressure and sound pressure levels with flow rate as measured on a flow bench for 2 samples prepared as described in Example 3 (designated 3A and 3B), and the same data for the as-installed muffler
25 (X), are provided in the Table below. Back pressure values are given in MPa, sound pressure values are in dBA, and flow rate is in slpm.

30

35

5		<u>FLOW RATE</u>			
		<u>283</u>	<u>566</u>	<u>849</u>	<u>1152</u>
	<u>Sample</u>				
	3A Back pressure	0.019	0.0635	0.115	0.1696
	Sound pressure	63	69.2	71.5	73.6
10					
	3B Back pressure	0.012	0.048	0.093	0.145
	Sound pressure	69.8	77	80.4	82.9
	X Back pressure	0.011	0.042	0.082	0.125
15	Sound pressure	69.3	78.6	82.8	85.9

These results indicate that mufflers made of the composite material of this invention exhibit greatly improved sound reduction compared to the originally installed muffler, while exhibiting only slightly higher back pressures.

Example 4

This example illustrates the preparation of a cylindrically-shaped composite part according to the invention having ceramic oxide fibers. The fibers provide additional reinforcement to the final part.

A mix of 4.66 parts by weight of ceramic spheres ranging in size from 10 to 125 micrometers (commercially available under the trade designation "Z-LIGHT W1012" from Zeelan Industries) and 1 part by weight epoxy resin ("SCOTCHCAST 265") was prepared as described in Example 1. To this mix was added an additional 4.2% by weight aluminosilicate ceramic fibers (commercially available under the trade designation "NEXTEL 312 CERAMIC FIBERS")

5 from the 3M Company). These fibers were obtained from "NEXTEL 312" ceramic fiber fabric by cutting it into lengths ranging from 1 to 8 mm. The fibers were dispersed in the mix by hand until they appeared to be uniformly distributed throughout the mix.

10 A sufficient quantity of the fiber-containing mix was used to fill a cylindrically-shaped mold measuring 6.98 cm in diameter x 11.43 cm in length with a center core measuring 5.02 cm in diameter to produce a hollow cylinder having a wall thickness of 0.95 cm. The mold was treated
15 with a fluorocarbon release agent ("REN RP79-1") before filling. The sample was then cured at 170°C for 2 hours and removed from the mold while still warm as described in Example 1. Following cure, the part was pyrolyzed and coated with silicon carbide as described in Example 1.

20

Example 5

This example illustrates preparation of yet another cylindrically-shaped composite part according to the invention.

25 A mix of 4.66 parts by weight of ceramic spheres ranging in size from 10 to 125 micrometers (commercially available under the trade designation "Z-LIGHT W1012" from Zeelan Industries of St. Paul, MN) and 1 part by weight epoxy resin ("SCOTCHCAST 265") was prepared as described in
30 Example 1. The mixture was used to fill a cylindrically-shaped aluminum mold measuring 5.08 cm in diameter x 10.16 cm in length. The mold was treated with a fluorocarbon release agent ("REN RP79-1") before filling. The cure, pyrolysis, and silicon carbide deposition steps were as
35 described in Example 1.

- 5 The porosity of the part following silicon carbide deposition was 32.7% (as measured according to the water displacement method described above). The weight gain of silicon carbide was 168 grams or 16.4%.

10 Example 6

 This example illustrates preparation of a cylindrically-shaped composite part having a double layer hollow core according to the invention.

- A hollow cylindrically-shaped part was prepared by
15 filling a cylindrically-shaped mold measuring 6.98 cm in diameter x 9.84 cm in length with a center core measuring 5.71 cm in diameter with a mixture of ceramic spheres ("Z-LIGHT W1600" spheres) and epoxy resin ("SCOTCHCAST 265") prepared in an 8:1 ratio in the manner described in Example
20 1. This sample was cured at 170°C for 2 hours. Following cure, the core was removed and a smaller core, measuring 4.76 cm in diameter, was positioned inside the cavity created by the first core. The gap between the sample and the smaller core was then filled with a second mixture of
25 ceramic spheres ("Z-LIGHT W1012") and epoxy resin in an 8:1 ratio. This mixture was cured for 2 hours at 170°C.

- Following the second cure step, the double layer sample was removed from the mold, coated with phenolic solution as described in Example 2, cured, removed from the
30 mold, and pyrolyzed and coated with silicon carbide as described in Example 1 to yield a double layer hollow cylinder. Such double layer hollow cylinders may be useful as candle filters.

35

5 Example 7

This example illustrates the preparation of a cylindrically-shaped composite part reinforced with ceramic fabric according to the invention.

10 Cylindrically-shaped articles similar to the articles described in Example 6 were prepared which incorporated reinforcing ceramic fabric scrims. Such scrims (which consist of open weave fabric) are commercially available under the designation "NEXTEL AF-8" fabric from the 3M Company, St. Paul, MN. AF-8 fabric is
15 woven from "NEXTEL 312" ceramic fiber. A section of "AF-8" weave measuring 9.84 cm x 22.86 cm was formed into a roll and placed inside the mold described in Example 6 measuring 6.98 cm in diameter x 9.84 cm in length such that the fabric conformed to the inner wall of the mold. An 8:1 mix
20 of ceramic spheres ("Z-LIGHT W1600") and epoxy resin ("SCOTCHCAST 265") was then prepared and poured into the mold. Cure was carried out as described in Example 1. The ceramic fiber netting became bonded to the outer edge of the part as the mixture of particles and resin cured around
25 it. The part was then pyrolyzed and coated with silicon carbide as described in Example 1. The final part showed a 42% increase in weight due to silicon carbide deposition.

Example 8

30 This example illustrates the preparation of a composite part according to the invention using powdered phenolic resin.

Disc-shaped samples were prepared from an 8:1 mix of ceramic spheres ("Z-LIGHT W1600") and epoxy resin
35 ("SCOTCHCAST 265") provided with an additional 1% by weight phenolic resin (commercially available under the trade

5 designation "DUREZ 29781" from Occidental Chemical Corp. of
Dallas, TX). The phenolic resin was a finely divided dry
powder; the addition of this powder was intended to
eliminate the need to dip coat a pyrolyzed part into
phenolic resin solution. The sample was cured, pyrolyzed,
10 and coated with silicon carbide as described in Example 1
to produce a solid cylindrically-shaped part.

Example 9

This examples illustrates the preparation of yet
15 another cylindrically-shaped composite part according to
the invention.

A cylindrically-shaped part was prepared from a mix
of 8 parts by weight ceramic spheres ("Z-LIGHT W1600") and
1 part by weight phenolic resin ("DUREZ 29781" dry powder)
20 as described in Example 1 except that the part was cured
for 12 hours at 170°C. The part was then pyrolyzed and
coated with silicon carbide as described in Example 1.

The part (3.5 cm diameter x 4.5 cm thick) was
tested for thermal shock resistance by heating the part in
25 a furnace to 1000°C (the point at which it glowed orange),
followed by immersion in water at room temperature (i.e.,
about 25°C). The part initially sank in the water, but
then floated with about a third of the part out of the
water until the pores filled with water and the entire part
30 sank. The portion above water retained an orange glow due
to the heat, indicating that there was a large thermal
gradient across the part.

The part was cycled in this manner five times.
Following cycling, the part remained dimensionally
35 unchanged except for the loss of a few surface particles,
indicating that the part is resistant to thermal shock

5 (i.e., it does not break or crack when exposed to rapid temperature changes).

Example 10

This example illustrates the thermal shock
10 resistance of a composite according to the present invention, as well as its use as a microwave receptor.

A mix of 3 parts by weight of aluminosilicate ceramic spheres ranging in size from 10-350 micrometers (commercially available under the trade designation "PQ-
15 SL150 EXTENDOSPHERES" from PQ Corporation, Valley Forge, PA) and 1 part by weight epoxy resin ("SCOTCHCAST 265") was prepared as in Example 1. The mix was used to fill a cylindrically shaped mold measuring 3.5 cm in diameter and 4.45 cm in length. The mold was treated with a
20 fluorocarbon release agent ("REN RP79-1") prior to filling the mold. The cure, pyrolysis, and silicon carbide deposition steps were as described in Example 1. The sample was heated in a furnace to 1000°C for about 10 minutes. It was then removed from the furnace and plunged
25 into water at room temperature. After several minutes the sample was removed from the water. No structural degradation was observed in the quenched sample.

The sample was heated to 1000°C and quenched in room temperature water four additional times. No
30 structural degradation was observed in the quenched sample. After the final (fifth) quenching, the sample was allowed to remain in the water overnight. The next day it was observed to have fractured in half along its long axis.

One of the halves of the fractured sample was
35 placed in a conventional microwave oven (commercially available under the trade designation "MICROFRIDGE, MODEL

5 MFM-1" from M&L Industries, Inc., Minneapolis, MN) and heated for twenty seconds. The microwave-heated sample was very hot to the touch.

Example 11

10 This example illustrates the resistance under load of a composite according to the invention to sagging and distortion. The load is applied at elevated temperatures and after the part has been subjected to elevated temperatures.

15 A flat plate of dimension 25.4 cm x 11.4 cm x 1.2 cm was cut from a block of epoxy resin plus aluminosilicate spheres prepared as described in Example 1. The flat plate was dipped into an aqueous solution of phenolic resin and then dried and heated as described in Example 2. The plate
20 was then subjected to pyrolysis and silicon carbide deposition as described in Example 1.

Next, the plate was loaded into a CM Rapid Temperature Furnace (commercially available from CM, Inc. of Bloomfield, NJ). Each corner of the plate was supported
25 by a 2.5 cm high, 1.2 cm diameter cylinder of a ceramic-ceramic composite material comprised of aluminoborosilicate ceramic fibers, a carbonaceous coating, and a silicon carbide coating (commercially available under the trade designation "SICONEX CERAMIC-CERAMIC COMPOSITE" from the 3M
30 Company). A 2.3 kg load was placed in the center of the plate. The furnace was ramped up to 1500°C over the course of about 1 hour and then maintained at 1500°C for 4 hours. The furnace controller was then turned off and the furnace allowed to cool. Inspection of the plate revealed that the
35 plate supported the load without any sagging or distortion during the heating cycle. The heating protocol was then

5 repeated and the plate again inspected after cooling. Once again, visual inspection revealed that the plate did not exhibit any sagging or distortion.

Following the second cooling step, the plate (supported by the ceramic composite cylinders ("SICONEX
10 CERAMIC-CERAMIC COMPOSITE")) was transferred to a lab bench where additional weight was placed on the center of the plate. The plate was able to support a load of 7.9 kg. When the load was increased to 9 kg, however, the plate broke into 3 pieces.

15 Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be limited to the illustrative embodiments set
20 forth herein.

5 What is claimed is:

1. A composite comprising

(a) ceramic filler particles in a carbonaceous matrix arranged in the form of a starved matrix microstructure having a surface available for coating; and

10 (b) a coating selected from the group consisting of silicon carbide, silicon nitride, and combinations thereof on a least a portion of the surface of said microstructure.

2. The composite of claim 1 wherein said filler
15 particles comprise substantially spherically-shaped particles.

3. The composite of claim 1 wherein said filler particles comprise substantially hollow particles.

20

4. The composite of claim 1 wherein said filler particles have an average size ranging from about 10 to about 1000 micrometers.

25 5. The composite of claim 1 wherein said filler particles have an average size ranging from about 10 to about 500 micrometers.

6. The composite of claim 1 wherein said filler
30 particles have an average size ranging from about 10 to about 325 micrometers.

7. The composite of claim 1 wherein said filler particles have a softening point greater than about 900°C.

35

5 8. The composite of claim 1 wherein said filler
particles have a softening point greater than about 1000°C.

9. The composite of claim 1 wherein said filler
particles comprise substantially hollow aluminosilicate
10 spheres.

10. The composite of claim 1 wherein said filler
particles comprise substantially solid aluminosilicate
spheres.

15 11. The composite of claim 1 having porosity
ranging from about 20 to about 60%.

12. The composite of claim 1 having porosity
20 ranging from about 30 to about 40%.

13. The composite of claim 1 wherein said
composite is in the form of a muffler.

25 14. The composite of claim 1 wherein said
composite is in the form of a filter.

15. The composite of claim 1 wherein said
composite is in the form of a catalyst support.

30 16. The composite of claim 15 further comprising
catalyst particles deposited on said support.

17. The composite of claim 1 wherein said
35 composite is in the form of an acoustic barrier.

5 18. The composite of claim 1 wherein said composite is in the form of kiln furniture.

 19. The composite of claim 1 wherein said coating is present in an amount ranging from about 25 to 35% by
10 weight.

 20. A composite comprising

 (a) substantially spherically-shaped ceramic filler particles in a carbonaceous matrix arranged in the form of
15 a starved matrix microstructure having a surface available for coating; and

 (b) a coating selected from group consisting of silicon carbide, silicon nitride, and combinations thereof on a least a portion of the surface of said microstructure.
20

 21. The composite of claim 20 wherein said filler particles comprise aluminosilicate spheres.

 22. A method for preparing a composite comprising
25 the steps of:

 (a) forming an article having a starved matrix microstructure with a surface available for coating from a mixture comprising ceramic filler particles and a first organic polymer binder;

30 (b) pyrolyzing said article to carbonize the binder while retaining the starved matrix microstructure of said article; and

 (c) depositing a coating of a material selected from the group consisting of silicon carbide, silicon
35 nitride, and combinations thereof on at least a portion of

5 the surface of said starved matrix microstructure to form
said composite.

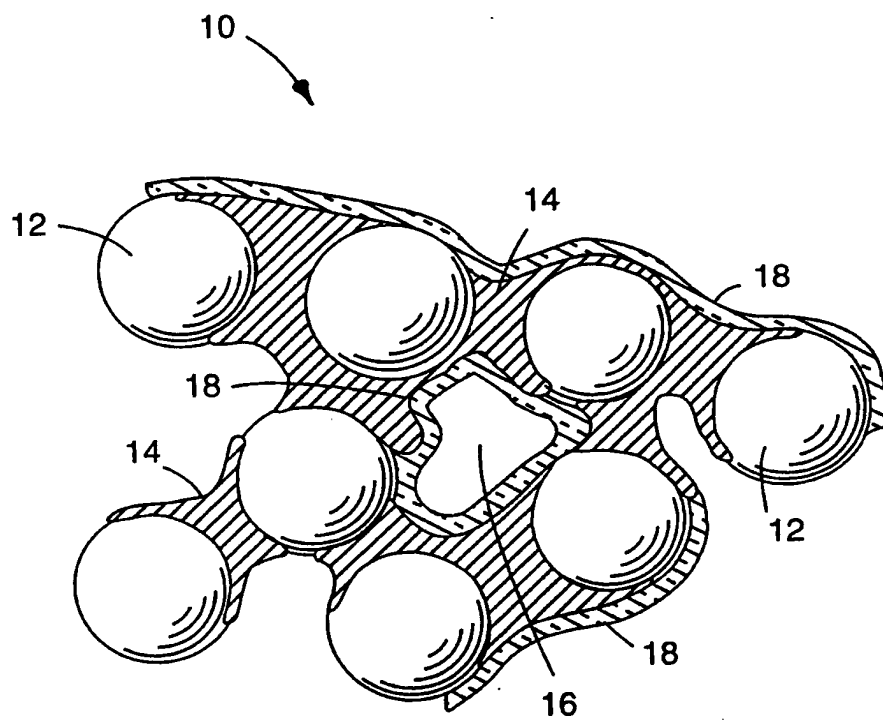
23. The method of claim 22 wherein said binder
comprises an epoxy resin.

10

24. The method of claim 22 wherein said binder
comprises a phenolic resin.

25. The method of claim 22 further comprising
15 applying a second organic polymer binder to said article
prior to pyrolysis.

26. The method of claim 22 comprising depositing
said silicon carbide or silicon nitride by chemical vapor
20 deposition.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/00151

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B41/87 C04B38/00 C22B9/02 G10K11/16 B01J27/224
B01J27/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 119, no. 12, 20 September 1993 Columbus, Ohio, US; abstract no. 123488y, KUROYANAGI AKIHIRO & AL. 'Manufacture of porous silicon carbide composites.' see abstract & JP,A,05 132 373 (TOKAI CARBON KK.) 28 May 1993	1, 14, 20, 22, 24, 26
A	FR,A,2 110 123 (KUREHA KAGAKU KOGYO KABUSHIKI KAISHA) 26 May 1972 see claims 1, 4, 5, 8-10	1
P, A	DE,A,42 28 433 (A.U.F. ADLERSHOFER UMWELTSCHUTZTECHNIK- UND FORSCHUNGSGESELLSCHAFT) 3 March 1994 see the whole document	1, 20
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 May 1995

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/00151

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CHEMICAL ABSTRACTS, vol. 108, no. 18, 2 May 1988 Columbus, Ohio, US; abstract no. 155431p, HASEGAWA KAZUHIRO & AL. 'Carbon foams with high strength and heat resistance' see abstract & JP,A,06 317 272 (KAWASAKI STEEL CORP.) 25 January 1988 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/00151

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DE-A-4228433	03-03-94	NONE	
US-A-3893928	08-07-75	NONE	